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Brent Tisserat

*United States Department of Agriculture*

Louis Reifschneider

*Illinois State University*

David A. Grewell

*Iowa State University, [dgrewell@iastate.edu](mailto:dgrewell@iastate.edu)*

Gowrishankar Srinivasan

*Iowa State University, [srigshan@iastate.edu](mailto:srigshan@iastate.edu)*

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# Effect of particle size, coupling agent and DDGS additions on Paulownia wood polypropylene composites

Brent Tisserat<sup>1</sup>, Louis Reifschneider<sup>2</sup>, David Grewell<sup>3</sup> and Gowrishanker Srinivasan<sup>3</sup>

## Abstract

Studies aimed at improving the tensile, flexural, impact, thermal, and physical characteristics of wood–plastic composites composed of Paulownia wood flour derived from 36-month-old trees blended with polypropylene were conducted. Composites of 25% and 40% w/w of Paulownia wood were produced by twin-screw compounding and injection molding. Composites containing 0–10% by weight of maleated polypropylene were evaluated and an optimum maleated polypropylene concentration determined, i.e., 5%. The particle size distribution of Paulownia wood filler is shown to have an effect on the tensile and flexural properties of the composites. Novel combination composites of dried distiller's grain with solubles mixed with Paulownia wood (up to 40% w/w) were produced and their properties evaluated. Depending on the composite tested, soaking composites for 872 h alters mechanical properties and causes weight gain.

## Keywords

Wood, particle reinforcement, thermal analysis, mechanical testing

## Introduction

The US wood–plastic composite (WPC) industry is projected to increase 13% a year to a value of \$5.3 billion by 2015 and similar annual increases thereafter are also seen in foreseeable future.<sup>1</sup> Much interest exists in the development of WPC that are more durable and cost-competitive compared to pre-existing commercial products.<sup>2–6</sup> The price of commercial WPC is dictated by the availability of high-quality sawdust and the current petroleum prices. Wood filler is derived from the waste products generated by lumber processing. In North America, ash, cedar, maple, oak, and pine wood flour (WF) are commonly employed in WPC, usually as mixture.<sup>6</sup> Wood waste material prices fluctuate on the basis of availability (housing demand) and the demand for their utilization.

Alternative woody biomass sources to provide WF are being developed.<sup>7–11</sup> Harvesting small-diameter trees obtained from forest under-stories or brush conditions offers biomass for both bio-energy needs as well as WF for WPC.<sup>11,12</sup> Short-rotational woody crops utilizing “fast-growing trees” grown on marginal lands are

another option to obtain woody biomass.<sup>7–11</sup> *Paulownia elongata* S.Y. Hu, Family Paulowniaceae, is an extremely fast-growing coppicing hardwood which is cultivated in plantations in China and Japan.<sup>12–14</sup> Paulownia wood (PW) is highly valued in the construction and furniture industries and has the following characteristics: light-weight, insect resistance, pale coloration, and heat resistance.<sup>12–14</sup> A Paulownia plot containing 2000 trees per hectare can yield up to

<sup>1</sup>Functional Foods Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, Peoria, USA

<sup>2</sup>Department of Technology, College of Applied Science and Technology, Illinois State University, Normal, USA

<sup>3</sup>Polymer Composites Research Group, Agricultural and Biosystems Engineering, College of Agriculture and Life Science, Iowa State University, Ames, USA

## Corresponding author:

Brent Tisserat, Functional Foods Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, Peoria, IL 61604, USA.  
Email: Brent.Tisserat@ars.usda.gov

150–300 tons of wood within 5–7 years. Paulownia trees are amenable to be established on marginal lands and have deep tap roots which make them drought resistant.<sup>12</sup> *Paulownia elongata*, *Paulownia kawakamii*, and *Paulownia tomentosa* are currently being grown and evaluated in the United States for their commercial wood properties.<sup>12</sup> Such trees offer an inexpensive source of woody biomass for energy and lumber which will also provide the wood wastes needed to manufacture WF.

Although the potential value of employing PW in WPC has recently been recognized,<sup>15–18</sup> much research still needs to be conducted to optimize the PW employment. Three core objectives were addressed in this study to optimize the use of PW flour (PWF) with polypropylene (PP) resins: selection of the coupling agent concentration, selection of suitable particle sizes, and determination of the properties of novel composites developed by mixing chemically dissimilar fillers. The utilization of PWF derived from juvenile trees, as a short-rotation woody tree crop, is a likely source of woody biomass needed by the US in the future. Thus, this study was conducted utilizing PWF derived from juvenile tree biomass (i.e., 36-month-old). Coupling agents are commonly used with wood fiber polyethylene (PE) and PP composites,<sup>9,16,18,19</sup> so the benefit of adding a maleated PP (MAPP) was examined to determine an optimal level of loading. In addition, because particle size may affect the performance of a WPC,<sup>9,20,21</sup> different sized particles of PWF were tested in composites. Where appropriate, the tensile and flexural properties of PW composites are benchmarked to virgin PP to demonstrate how PW composites compares as a WF reinforcement.

Because WPC employing PW has been demonstrated to have excellent mechanical properties,<sup>17,18</sup> preliminary tests were conducted to determine the benefit of mixing two dissimilar bio-fillers, i.e., dried distiller's grain with solubles (DDGS) and PW with PP. It is the contention of this study to develop a "novel" composite containing part "superior" and "inferior" fillers, which exhibits mechanical properties superior to that employing the "inferior" fillers. DDGS was selected because its composition (high in protein) is similar to most seed press cakes which are inexpensive and abundant feed stocks.<sup>22,23</sup> Wood fillers composed of cellulose (40–45%), lignin (20–30%), protein (~1–2%), and solvent extractables (~3–12%) are the most accepted bio-filler employed in lignocellulosic plastic composites (LPC). In contrast, DDGS and press cakes contain high concentrations of protein (20–35%) and vegetable oils (~8–12%), and have much lower cellulose (11–25%) and lignin (3–15%) levels.<sup>22,23</sup> Few studies have been conducted employing DDGS or press cakes as a bio-filler with thermoplastic resins.<sup>24–26</sup>

Utilization of DDGS and press cakes fillers have resulted in composites with poor mechanical properties.<sup>24–27</sup> Recently, Tisserat et al.<sup>26</sup> reported that a composite high-density polyethylene (HDPE) with a solvent-treated DDGS (STDDGS) was superior to an HDPE with conventional DDGS in terms of their tensile and flexural properties.

Finally, water immersion tests were administered on these PWF composites to evaluate their environmental durability. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted on PW composites to evaluate their thermal properties and the implications these may have on selecting processing conditions for the bio-fiber reinforcements.

In order to better understand the motivation for the scope of this work, the theoretical foundation of the three core objectives of this study is summarized here. The MAPP is added to improve the adhesion of the hydrophobic wood particles to the hydrophilic PP matrix.<sup>19</sup> The main advantage of the MAPP will be to minimize incompatible surfaces, or discontinuities, between the reinforcement and the matrix. The net effect is to reduce the formation of microscopic cracks that can ultimately lead to failure either in tension or during impact. Thus, it is expected that the addition of MAPP will improve tensile strength. Further, the addition of MAPP is expected to have a positive effect on impact strength because it will serve to minimize crack propagation. The mechanical property of modulus, on the other hand, is a low deformation process that does not lead to significant crack propagation; thus, the modulus is not expected to change significantly with the addition of MAPP. The addition of fiber reinforcements is expected to increase the modulus as the fibers have a higher modulus than the matrix and they will impede the small-scale deformation of the spherulites in the matrix.

The second objective of the study involves documenting the effect of particle size on relevant mechanical properties. An important point to make regarding the compositions employed in this study is that the mass percentage of the filler remains constant as the average particle size changes. Consequently, if one assumes the particles have a spherical shape, then as the particle size decreases by a factor of two the area of contact between the filler and the matrix doubles. This increase in contact area of the filler and the matrix indicates that as the mean particle size of the filler decreases the tensile strength and impact strength may drop due to an increase in the number of locations where microscopic cracks may form. Further, as the particle size in the filler decreases they become more on the order of the size of the spherulites in the matrix. The particle sizes in this study range from around 600  $\mu\text{m}$  on the large size to as small as 75  $\mu\text{m}$ ,

**Table 1.** Sieve information and particle distribution percentages.

Sieve No.	Sieve opening ( $\mu\text{m}$ )	Particle sizes ( $\mu\text{m}$ ) <sup>a</sup>	Composition (%) <sup>b</sup>	Length ( $\mu\text{m}$ ) <sup>c</sup>	Diameter ( $\mu\text{m}$ ) <sup>c</sup>	Aspect ratio
30	600	$\geq 600$	0.8	—	—	—
40	425	425–600	37.4	1178	441	2.7
50	300	300–425	31.2	1074	333	3.2
60	250	250–300	11.7	761	156	4.9
80	180	180–250	4.5	491	124	4.0
140	106	106–180	6	367	112	3.3
200	75	75–106	4.5	143	73	2.0
>200	$\leq 75$	$\leq 75$	3.9	—	—	—
$\geq 40$	$\leq 600$	$\leq 600$	—	—	—	—

<sup>a</sup>Theoretical particle size collections.<sup>b</sup>Distribution of PW particles obtained from a 1-mm Wiley milled screen and sieved through the Ro-Tap Shaker.<sup>c</sup>Actual particle measurements. Average of 20 measurements presented.

refer to Table 1. Spherulites for PP can vary in size from around 10  $\mu\text{m}$  to around 200  $\mu\text{m}$ .<sup>28</sup> This size parity indicates that the addition of the smaller filler particles will have less influence to retard the deformation of the spherulites during loading and thus tend to decrease the modulus compared to fillers that are significantly larger in size.

The third objective of the study is to assess if fillers with different surface chemistry properties can synergistically work to improve the mechanical properties of the composite. In this case, relatively low-cost filler DDGS is examined to see if it can be used in conjunction with PW to make an acceptable reinforcement.

## Experimental

### Materials

The PP employed was Pro-fax SB891 (Lyondellbasell, Equistar Chemicals LP, Houston, TX). It had a melt-flow index of 35 g/10 min, a density of 0.90 g/cm<sup>3</sup>, and a melting temperature of 165°C. The coupling agent was a MAPP supplied by Equistar Chemicals LP (product code NP 507-03) and had a melting point of 155–165°C with approximately 1% maleic anhydride by weight grafted on the PP.

*P. elongata* wood material was obtained from 36-month-old trees grown in Fort Valley, GA. PW shavings were milled with a Thomas-Wiley mill grinder, (Model 4, Thomas Scientific, Swedesboro, NJ). Filler particles were milled successively through 4-, 2-, and 1-mm diameter stainless screens. Particles were then sized through a Ro-Tap<sup>TM</sup> Shaker (Model RX-29, Tyler, Mentor OH) employing sieve mesh sizes of #30, #40, #50, #60, #80, #140, and #200 US Standards (Newark Wire Cloth Company, Clifton, NJ). Particles from the #40, #60, #140, and #200 sieves were blended with PP to produce composites for the particle size study

(see Table 1). All of the particles that passed through the #30 sieve were collected and used to create the standard filler employed in this study. These particles were all smaller than 600  $\mu\text{m}$ . This composition will be referred to as the “ $\geq$ #40” filler. There were other tests done using a subset of the particles that only passed through specific sieves. All formulations with their respective particle sizes are shown in Table 1. The ball ground PW (BGPW) flour was obtained from 1-mm milled PWF and ground in a laboratory bench top ball mill (Model 801CVM, U.S. Stoneware, East Palestine, OH) to obtain fine powder. BGPW flour was sieved through a #200 screen and designed hereafter as finer than #200 mesh, or “>#200” and is composed of particles that are smaller than 75  $\mu\text{m}$ . The final step in the PW preparation included oven drying each screened fraction for 48 h at 100°C.

DDGS was obtained as commercial animal feed pellets (Archers Daniel Midland Co., Decatur, IL). The pellets were mill ground and sieved through a #30 mesh to obtain a standard filler mixture of  $\geq$ #40, as previously discussed. To examine what effect the oils in the DDGS have on the mechanical properties of the composites, the vegetable oils were extracted from the milled DDGS with hexane and the polar extractables were subsequently removed with acetone by employing a Soxhlet extractor. Throughout this paper DDGS refers to the original DDGS and STDDGS refers to the solvent-treated DDGS. In some cases, the polar extractables in the PW were extracted with acetone to provide a solvent-treated PW, hereafter labeled as STPW.

### Material preparations and testing

Table 2 summarizes the various formulations used in this study. Composite blends were extruded with a 27-mm co-rotating intermeshing twin-screw extruder,



**Table 2.** Weight percentages of Paulownia wood formulations.

Treatments	PP/MAPP/DDGS/ STDDGS/PW/STPW
PP	100/0/0/0/0/0
PP-MAPP	95/5/0/0/0/0
PP-25PW	75/0/0/0/25/0
PP-PW-1%MAPP	74/1/0/0/25/0
PP-PW-3%MAPP	72/3/0/0/25/0
PP-PW-5%MAPP	70/5/0/0/25/0
PP-PW-7%MAPP	68/7/0/0/25/0
PP-PW-10%MAPP	65/10/0/0/25/0
PP-#40PW-MAPP	70/5/0/0/25/0
PP-#60PW-MAPP	70/5/0/0/25/0
PP-#140PW-MAPP	70/5/0/0/25/0
PP-#200PW-MAPP	70/5/0/0/25/0
PP-25BGPW-MAPP	70/5/0/0/25/0
PP-25PW-MAPP	70/5/0/0/25/0
PP-25STPW-MAPP	70/5/0/0/0/25
PP-25DDGS-MAPP	70/5/25/0/0/0
PP-25STDDGS-MAPP	70/5/0/25/0/0
PP-20PW/5STDDGS-MAPP	70/5/0/5/20/0
PP-12.5PW/12.5STDDGS-MAPP	70/5/0/12.5/12.5/0
PP-20PW/20STDDGS -MAPP	55/5/0/20/20/0
PP-40PW-MAPP	55/5/0/0/40/0

PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood; STPW: solvent-treated Paulownia wood; DDGS: dried distiller's grain with solubles; STDDGS: solvent-treated dried distiller's grain with solubles.

with a length/diameter ratio of 40 (Model ZSE-27 American Leistritz Extruder Corporation, Branchburg, NJ). The barrel had 10 different zones, each 90 mm long, which were temperature controlled from 100°C to 200°C. Pre-mixed fillers and PP were dry blended in 1 gallon-resalable plastic bags. Materials were then transferred into a single drive feeder (Flex-Tuff Model 306, Schenck/AccuRate, Whitewater, WI) and fed into the extrusion feeder at the rate of 100 g/min. Extruder screw speed was set at 100 r/min. Extruded strands were cooled by immersion in a water bath and then pelletized with a strand pelletizer (Model 60E, Automatick Plastics Machinery GmbH, Grosseothheim, Germany).

Molding was conducted with a 30-ton molding machine (Model Engel ES 30, Engel Machinery Inc., York, PA) using an ASTM family mold to obtain a Type I, Type V, and flexural bar set. Set point temperatures (°C) for the four zone injection molding barrel were as follows: feed = 160; compression = 166; metering = 177; and nozzle = 191. The mold temperature was 37°C. Type I bars were used for the tensile strength property tests. The flexural bars were used to

evaluate flexural properties and also used to make impact strength measurements. Type V bars were used to evaluate changes resulting from exposure to water: weight change and tensile mechanical properties of the composites.

Samples were conditioned for approximately 240 h at standard room temperature and humidity (23°C and 50% RH) prior to any test evaluations. Injection-molded specimens, ASTM D638 Type I tensile bars, were tested for tensile modulus and strength using a universal testing machine (UTM) (Model 1122, Instron Corporation, Norwood, MA). The speed of testing was 50 mm/min, which is 1 mm/mm/min strain rate at the start of the test. Three-point flexural tests were carried out according to ASTM D790 specification with an Instron UTM Model 1122. The flexural tests were conducted on molded flexural bars following Procedure B with a rate of straining of the outer fiber equal to 0.1 mm/mm/min. In this study, the support span was 50.8 mm, the width and thickness of the test specimens were 6.25 mm and 3.17 mm, respectively. Notched impact tests were conducted with an IZOD impact tester (Model Resil 5.5, P/N 6844.000, CEAST, Pianezza, Italy) conformed to ASTM D256-84. Five specimens of each formulation were tested and their average values and standard errors calculated; treatments were compared using the Duncan's Multiple Range test ( $p \leq 0.05$ ).

The Type V tensile bars injection molded for each composite were dried in an oven for 48 h at  $80 \pm 2^\circ\text{C}$  and weighed. Tensile bars were placed in distilled water at room temperature for 872 h. At predetermined time intervals, the specimens were removed from the distilled water, the surface water was blotted off with paper towels, and their wet mass was determined. Water absorption, measured as weight gain percentage, was computed using the following formula

$$\text{Weight gain (\%)} = (m_t - m_o)/m_o \times 100 \quad (1)$$

where  $m_o$  denotes the oven-dried weight and  $m_t$  denotes the weight after soak time  $t$ .

DSC of molded specimens was conducted with an Auto DSC-7 calorimeter with a TAC/DX controller (TA Instruments, New Castle, DE). Samples of 5–7 mg were weighed and sealed hermetically in aluminum DSC pans. First, the calorimeter was programmed to increase the temperature from 0°C to 180°C at a rate of 10°C/min, kept isothermal for 3 min. Second, the samples were cooled to  $-50^\circ\text{C}$  at a rate of 10°C/min. Finally, the samples were heated to 180°C from  $-50^\circ\text{C}$  to 180°C at the same rate. Data from the second heating cycle were used to determine the melting temperature ( $T_m$ ) and enthalpy of melting ( $\Delta H_m$ ) for PE-PW blended samples. Data from the second cooling cycle

were used to determine the crystallization temperature ( $T_c$ ) and crystallization enthalpy ( $\Delta H_c$ ) for the same samples. The heat flow rate corresponding to the crystallization of PP in composites was corrected for the content of the WF and MAPP. The value of crystallization heat was also corrected for the crystallization heat of MAPP. The degree of crystallinity ( $\chi_c$ ) of the PP matrix was evaluated from the following relationship<sup>29</sup>

$$\chi_c = \Delta H_{\text{exp}} / (\Delta H \times W_f) \times 100 \quad (2)$$

where  $\Delta H_{\text{exp}}$  is the experimental heat of fusion ( $\Delta H_m$ ) or crystallization determined by DSC,  $\Delta H$  is the assumed heat of fusion or crystallization of fully crystalline PP (204 J/g), and  $W_f$  is the weight fractions of PP in the composites.

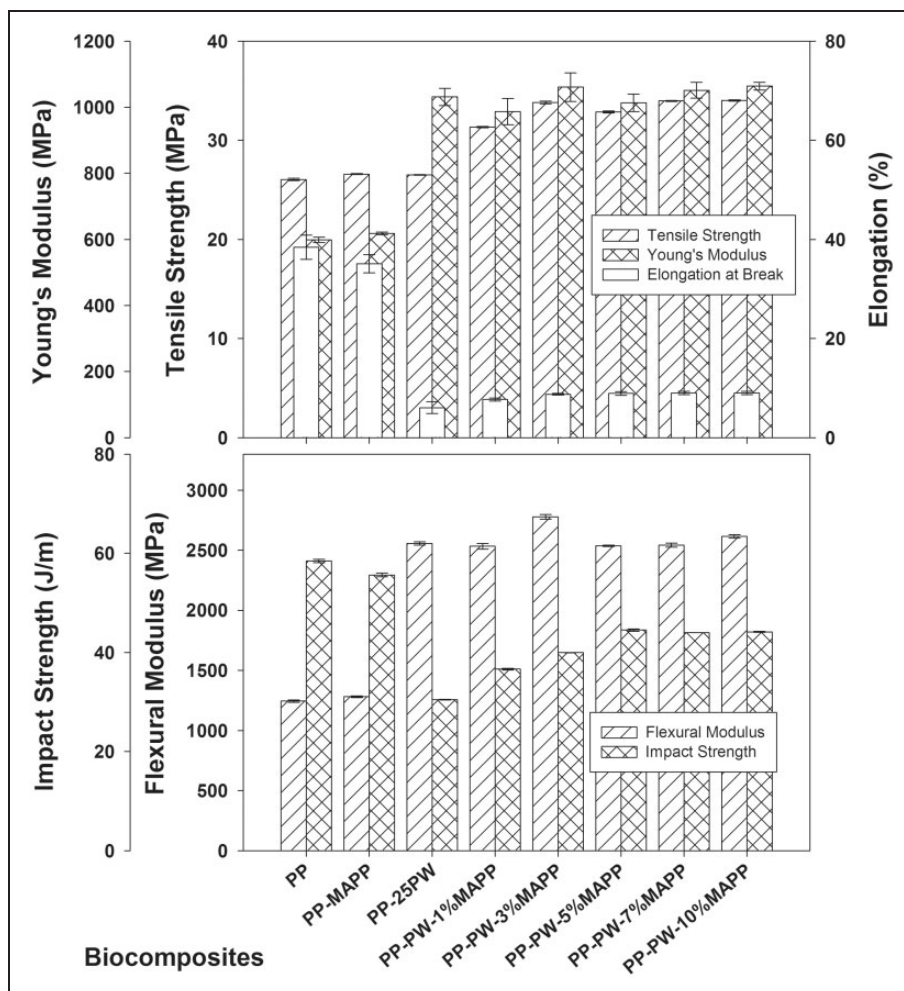
TGA was performed to determine the thermal characteristics of the composites. The TGA test was conducted using a Model 2050 TGA (TA Instruments)

under nitrogen at a scan rate of 10°C/min from room temperature to 600°C. A sample of  $\approx 7.5$  mg was used for each run. Data were analyzed using the TA Advantage Specialty Library software (TA Instruments). The derivative TGA (wt%/min) of each sample was obtained from the software.

## Results and discussion

### Influence of MAPP concentrations

MAPP is often employed to improve the adhesion between the bio-based filler and plastic.<sup>10,19,26,27,29–31</sup> Coupling agents act as intermediates to bind hydrophobic polyolefins to hydrophilic lignocellulosic materials (e.g., wood or DDGS). The mechanical testing results of the effect of the coupling agent concentration are graphically presented in Figure 1. Results include tensile strength ( $\sigma_u$ ), Young's modulus (E), elongation



**Figure 1.** Effect of PP-PW composites treated with various coupling agent (MAPP) concentrations on their tensile, flexural and impact strength properties compared to the control material PP.

PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood.

strain at breaking (%El), modulus of elasticity in bending ( $E_b$ ), and Izod notched impact strength. The  $\sigma_u$  for the PW composite made without the MAPP coupling agent is comparable to neat PP (Figure 1). The  $\sigma_u$  of the composites is improved by approximately 25% compared to the neat PP when the coupling agent MAPP is added. Other studies have shown this trend.<sup>18,19,26,27,29–31</sup> Tensile strength is a measure of the stress load a material can support before generating voids that lead to crazing of the material and ultimate failure. The  $\sigma_u$  increase is attributed to better transfer of stress between the hydrophobic wood fiber and the hydrophilic PP matrix due to the chemical coupling. The improved surface contact between the wood and the PP also leads to fewer locations for microscopic cracks to form and this retards failure due to crack formation which limits tensile strength. The inclusion of 25% PWF reinforcement dramatically improved the elastic modulus; even without adding the coupling agent, with an increase in  $E$  values of 75% over the neat PP occurs. The modulus improves due to the presence of the stiffer wood particles that impede the deformation of the spherulites in the matrix. Modulus is a low-deformation mechanical property that is not affected by poor adhesion of the filler with the matrix. Consequently, when MAPP is added there is relatively little increase in stiffness over the already improved modulus. The third property summarized that Figure 1 is the percentage elongation at break in tension, which is largely a deformation property. The %El for all the wood composites was much lower than the neat PP. Any reduction in the adhesion of material at the matrix/composite interface provides a location where microscopic cracks form. This leads to crazing within the matrix and subsequent failure at relatively low elongations. The addition of MAPP beyond 3% helped improve the elongation by a modest amount, but apparently there were still numerous locations where the discontinuity of the hydrophobic wood fiber and the hydrophilic PP existed.

The trends for the  $E_b$  follow that of the  $E$ . The combination of the improved resistance to compression and the comparable improved strength in tension yields an  $E_b$  that is over twice as stiff as the neat PP (Figure 1). The notched impact strength measured in this study involved the propagation of a crack due to an existing notch. The factors that influence impact strength in a composite are complex. There are several mechanisms that affect the energy dissipated during crack propagation: plastic deformation of the matrix in front of the crack tip, fiber debonding from the matrix, and fiber breakage and pull-out from the matrix.<sup>28,32,33</sup> Further, the plastic deformation of the matrix in the area in front of the propagating crack can be influenced by the degree of crystallinity present in the matrix.

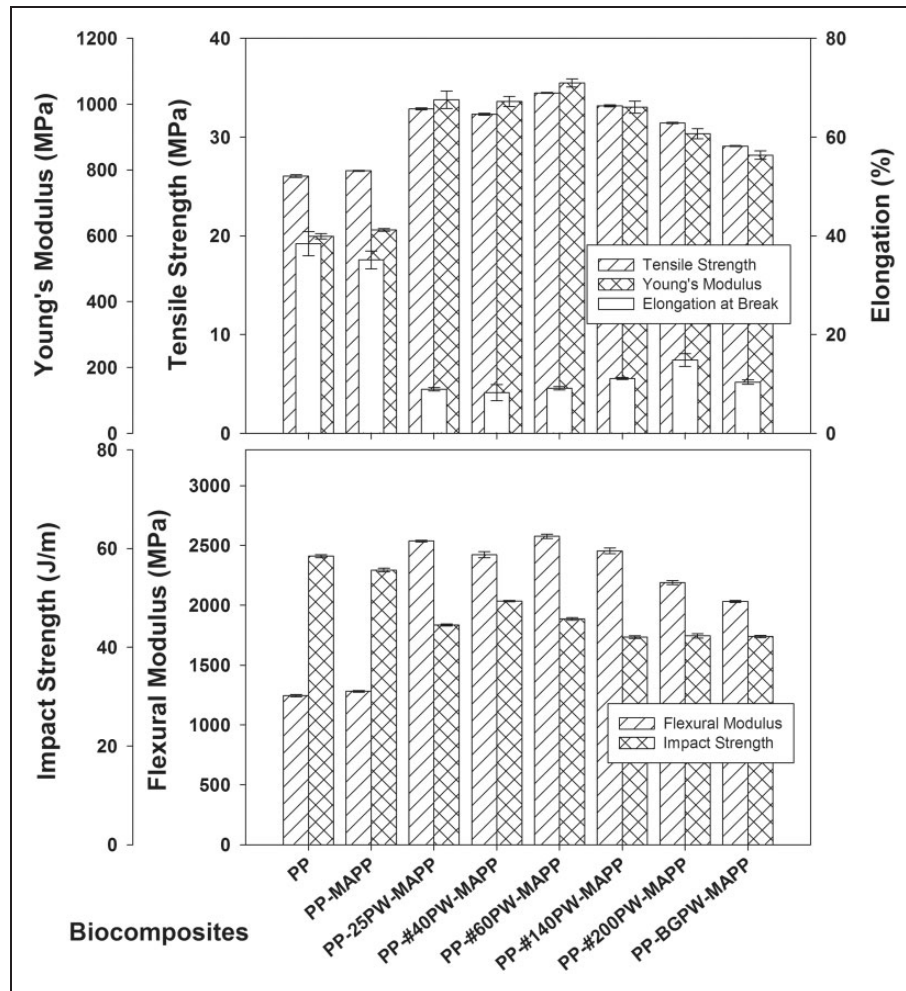
The addition of PW at 25% without any MAPP (PP-25PW) exhibited impact strength of 52% to that of the neat PP value. The impact strength values are improved by 10% with the addition of 1% MAPP. The likely cause is the improved fiber bonding with the matrix. However, as more MAPP is added, the benefit plateaus at 5% MAPP (PP-PW-5%MAPP) with values that were only 69% of the neat PP. The diminishing return may be due to some critical level of bonding being reached with the available fiber. Another factor that limits the benefit of adding MAPP is the contrary effect of the increase in the degree of crystallinity due to more MAPP being added (Table 3). It is known that a higher percentage of crystallinity in a semi-crystalline polymer will lower the impact energy.<sup>33</sup> The DSC data in this study (Table 3) show there is an increase in the degree of crystallinity present in the matrix as wood fiber and MAPP are added. The neat PP used in this study had degree of crystallinity of 35%, while the composite made with 25% PW and 7% MAPP had a degree of crystallinity of 38%. In summary, the addition of higher concentrations of MAPP beyond a critical level was not beneficial. The addition of 3–5% MAPP in the formulation yielded an optimal improvement of most mechanical properties. Thus, for the balance of the study, a MAPP formulation concentration of 5% MAPP was used.

### *Influence of particle size*

The particle size effect on the mechanical properties of the PW composites is graphically illustrated in Figure 2. It is important to note in the following discussion that there is an inverse relationship between the particle size of the wood fiber and the interfacial area of contact between the wood fiber and the PP matrix. For example, 200  $\mu\text{m}$  particle size filler will have twice the interface area of 400  $\mu\text{m}$  size filler because each composition has the same mass of PW when added to the matrix. Further, the theoretical particle sizes based upon the sieve openings differ considerably from the actual particle sizes. The sieve openings indicate particles that are nearly spherical in size when in fact the particles are approximately cylindrical in shape with length to diameter ratios of about 4. The aspect ratio of fiber reinforcements do have an effect of the ability of the reinforcement to interact with the matrix, but this is beyond the scope of this study. Table 1 summarizes the particle size distribution obtained from the various sieve openings used in this study.

Although the  $\sigma_u$  of the composites for all the particle sizes studied is greater than the neat PP, the lowest  $\sigma_u$  occurred when the smallest particle sizes were employed (PP-#200PW-MAPP containing  $\leq 75 \mu\text{m}$  particles). The likely explanation for this trend is the increased





**Figure 2.** Effect of PP-PW composites composed of various particle sizes on their tensile, flexural and impact strength properties compared to the control material PP.

PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood; BGPW: ball ground Paulownia wood.

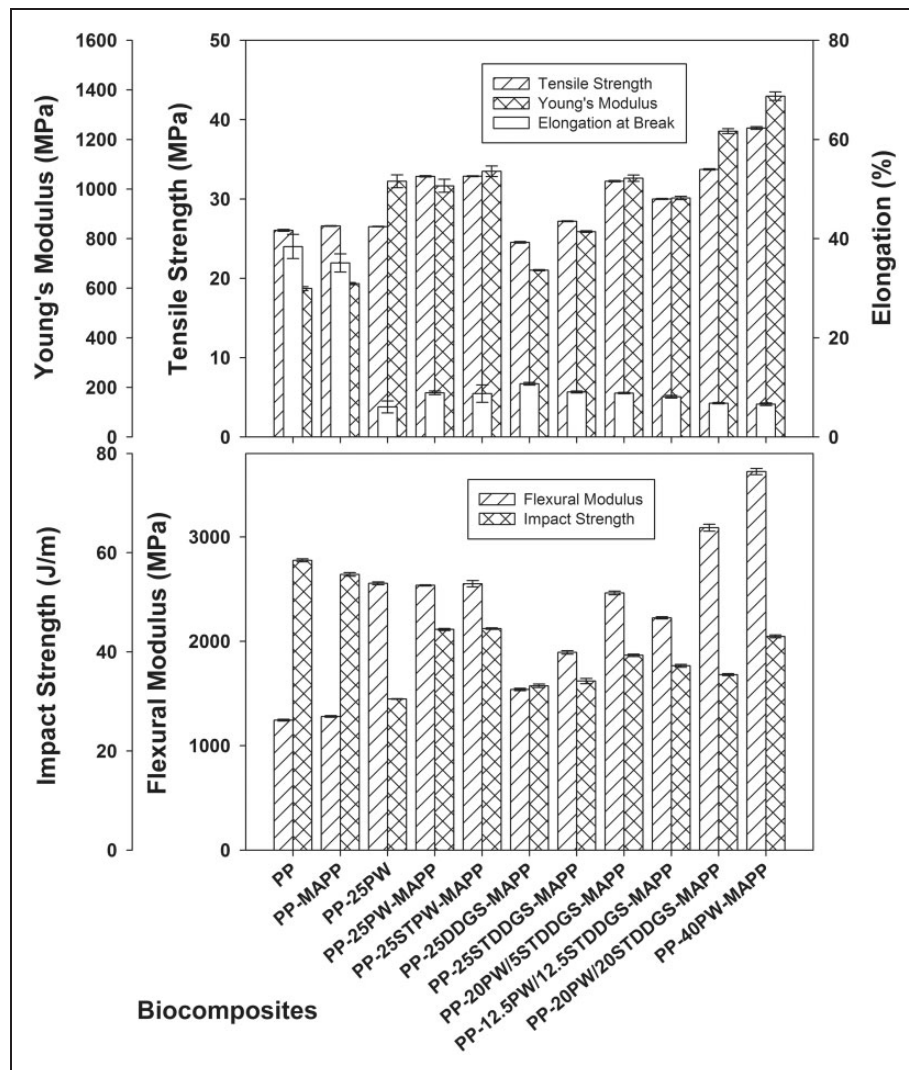
interfacial area between the incompatible hydrophilic wood and the hydrophobic PP matrix. Because  $\sigma_u$  depends upon the composite sustaining a load over a relatively large deformation without initiating cracks, the added interfacial contact with more particles, i.e., the smaller particle loading will likely permit more micro cracks to form, thus limiting the strength. The peak in tensile strength occurs with the PP-#60PW-MAPP composite containing 250–300  $\mu\text{m}$  particles; similar  $\sigma_u$  occurred from the PP-25PW-MAPP composite containing  $\leq 600 \mu\text{m}$  particles probably because this PW composition consists of a wide range of large and small particles.

The  $E$  is related to the deformation of the spherulites in the matrix. Smaller PW particles apparently offer less interference than the larger PW particles in the matrix. The peak  $E$  in this study occurs with the PP-#60PW-MAPP composite composed of 250–300  $\mu\text{m}$  particles. A slight reduction in modulus occurs with the

PP-#40PW-MAPP composite containing 425–600  $\mu\text{m}$  particles may be due to the fact that there are fewer particles present in this formulation than the PP-#60PW-MAPP composite and thus more opportunity for the spherulites to deform and lower the modulus. The  $E_b$  trends are similar to the  $\sigma_u$  and the  $E$  trends for the similar reasons as given in the previous discussion.

The %El results exhibit a contrary trend to that seen for the modulus data. Smaller particles allow for a larger deformation before failure. This occurs, however, at a lower stress as the  $\sigma_u$  numbers decline in composites containing smaller particles. The smaller particles also lower the modulus of the composite. In effect, the composite (PP-25BGPW-MAPP) is made more plastic due to the particles being on the order of size of the spherulites in the matrix which can range from 20  $\mu\text{m}$  to 100  $\mu\text{m}$  for PP.<sup>33</sup>

The impact strength results are difficult to summarize due to the complex nature of the phenomenon



**Figure 3.** The tensile, flexural and impact strength properties of dissimilar filler mixtures compared to the control material PP. PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood; STPW: solvent-treated Paulownia wood; DDGS: dried distiller's grain with solubles; STDDGS: solvent-treated dried distiller's grain with solubles.

as outlined in the previous discussion. The smaller particle sets, less than  $106\mu\text{m}$ , exhibit the lowest impact energy compared to the three other larger particle size composites. This may be due to the increase in the interfacial area and available locations for cracks to propagate or perhaps to fiber aspect ratio of the smaller particles differed from the larger particles.

Overall, these results are similar to that found by other investigators, who found that wood-PP composites containing larger particles exhibited higher mechanical properties and impact strength than wood-PP composites composed of smaller particles.<sup>9,20</sup> In summary, the PP-25PW-MAPP formulation shown in Figure 2 yielded excellent mechanical properties compared to the other particle size composites. The PP-

25PW-MAPP composite contained a wide distribution of particle sizes ( $\leq 600\mu\text{m}$  particles) that are distributed as shown in Table 1 and coincidentally was the simplest particle fraction to prepare. This particle size filler mixture containing derived from  $\geq \#40$  mesh fractions is recommended for future uses.

### Influence of mixing different fillers

The mechanical properties resulting from the blending of DDGS with PW are summarized in Figure 3. The STDDGS composite (PP-25STDDGS-MAPP) was superior to DDGS composite (PP-25DDGS-MAPP) in terms of the  $\sigma_u$ ,  $E$ , and  $E_b$  values showing increases of 10%, 20%, and 20%, respectively. However, little differences were seen for impact

**Table 3.** DSC and TGA thermal data for composites.

Composition	DSC data			TGA degradation peaks		
	$T_c$ (°C)	$T_m$ (°C)	$\chi_c$ (%)	Peak 1	Peak 2	Peak 3
PP	117.6	162.6	35.2	—	—	452.2
PP-MAPP	117.6	163.3	34.8	—	—	452.2
PP-25PW	119.4	163.7	38.8	280.3	346.7	455.9
PP-PW-1%MAPP	120.6	165.0	36.7	281.4	347.6	455.4
PP-PW-3%MAPP	119.8	166.1	35.4	278.4	347.7	456.7
PP-PW-5%MAPP	120.6	164.8	38.3	276.6	347.3	456.9
PP-PW-7%MAPP	120.5	164.4	38.2	281.9	348.5	455.7
PP-PW-10%MAPP	120.5	164.0	36.6	290.1	349.6	458.3
PP-#40PW-MAPP	119.1	164.2	37.2	284.1	348.7	454.4
PP-#60PW-MAPP	120.1	164.7	35.9	272.9	346.9	454.0
PP-#140PW-MAPP	121.1	164.5	37.7	273.9	346.4	456.9
PP-#200PW-MAPP	122.0	164.5	39.2	278.1	348.1	458.2
PP-25BGPW-MAPP	121.0	163.5	37.2	280.1	344.3	455.7
PP-25PW-MAPP	120.6	164.8	38.3	276.6	347.3	456.9
PP-25STPW-MAPP	120.0	164.3	37.3	274.6	348.4	458.1
PP-25DDGS-MAPP	122.3	163.2	37.4	274.3	321.4	456.5
PP-25STDDGS-MAPP	122.4	163.9	34.8	276.1	322.9	456.0
PP-20PW/5STDDGS-MAPP	120.9	163.8	36.8	278.9	345.7	456.5
PP-12.5PW/12.5STDDGS-MAPP	120.6	165.5	35.8	279.9	344.5	456.2
PP-20PW/20STDDGS-MAPP	121.6	165.1	36.9	275.7	343.5	458.9
PP-40PW-MAPP	121.0	165.1	37.2	277.9	345.4	457.3

DSC: Differential scanning calorimetry; TGA: Thermogravimetric analysis; PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood; STPW: solvent-treated Paulownia wood; DDGS: dried distiller's grain with solubles; STDDGS: solvent-treated dried distiller's grain with solubles; BGPW: ball ground Paulownia wood.

strength and elongation values in composites using these two fillers sources. It is of interest to note that the  $E$  of the STDDGS composite significantly exceeded the  $E$  of the DDGS composite as shown in Figure 3; this is probably attributed to the removal of oils in the STDDGS material. The presence of oil in the DDGS acts as a plasticizer that lubricates the relative motion of spherulites, hence lowering the modulus. In addition, the  $E_b$  values greatly improved in composites with STDDGS versus those containing DDGS, refer to Figure 3. Hereafter, the STDDGS was used in formulation mixing to obtain a combination LPC. The LPC containing STDDGS (PP-STDDGS-MAPP) exhibited  $\sigma_u$ ,  $E$ , %El,  $E_b$ , and impact strength values that were +4%, +38%, -76%, +52%, and -42%, respectively, of the values obtained from neat PP. In comparison, WPC containing PW (PP-25PW-MAPP) exhibited  $\sigma_u$ ,  $E$ , %El,  $E_b$ , and impact strength values that were +26%, +70%, -76%, +104%, and -24%, respectively, of the values obtained from neat PP. The benefit of removal of extractables in order to obtain superior fillers has been previously documented.<sup>10,26,27</sup> However, when PW was given a solvent extraction treatment, no

benefit was obtained in terms of the resulting mechanical properties compared to untreated PW (Figure 3). Therefore, untreated PW only was employed in preparation of combination filler LPC. Others have shown that the flexural behavior of the composites can vary significantly with the type of filler and coupling agent employed.<sup>10,31</sup>

LPC containing a combination of STDDGS with PWF showed superior mechanical properties (except elongation values) compared to LPC composed of only STDDGS (Figure 3). LPC composed of 12.5% STDDGS and 12.5% PW (PP-12.5PW/12.5STDDGS-MAPP) exhibited  $\sigma_u$ ,  $E$ , %El,  $E_b$ , and impact strength values that were +15%, +61%, -79%, +78%, and -36%, respectively, of the values obtained from neat PP. These values compare well with PP-25STDDGS-MAPP but were slightly less than the values obtained from PP-25PW-MAPP (Figure 3). When only 5% STDDGS was mixed with 20% PW (PP-20PW/5STDDGS-MAPP), the resulting LPC exhibited  $\sigma_u$ ,  $E$ , %El,  $E_b$ , and impact strength values that were +24%, +74%, -69%, +97%, and -33%, respectively, of the values obtained from neat PP.

These values compared favorably to PP-25PW-MAPP and PP-25STDDGS-MAPP. All composites had higher  $E_b$  values than the neat PP and PP-MAPP blends. However, the highest flexural modulus values were obtained employing the highest loading contents (PP-40PW-MAPP and PP-20PW/20STDDGS-MAPP). These results suggest that a useful inexpensive LPC composed of both DDGS and PW is feasible. High mechanical, flexural, and impact properties are obtainable from mixing STDDGS with PW, over that of employing a composite containing STDDGS only.

### Water absorption responses

Figure 4 shows the long-term water absorption (872 h) as a function of time for the various LPCs at room temperature. All composites absorbed water during the incubation period, saturation levels may occur in the PW composites but not with the DDGS composites (Figure 4). The PP and PP-MAPP samples exhibited considerably less weight gain (i.e., less than a 1% increase) after the immersion incubation time compared to the composites (Figure 4). Absorption of water by composites is a crucial factor in determination of the ability of biocomposite to be commercially utilized.<sup>34,35</sup> Inclusion of the MAPP coupling agent to the formulation generally produces a composite that was more resistant to water absorption than a composite devoid of MAPP. For example, PP-25PW and PP-25PW-MAPP exhibited weight gains of 2.7% and 2.2%, respectively. Other investigators have reported that inclusion of maleated olefins with the composite blend considerably reduces water absorption when using bio-fillers such as poplar wood, loblolly pine wood, sisal fiber, or wheat straw.<sup>34–38</sup> Particle size of PW in composite blends did influence weight gain (Figure 4). Composite blends composed of smaller particles (PP-#200PW-MAPP and PP-25BGPW-MAPP) exhibited less weight gain than composites that contained larger particles (PP-#40PW-MAPP and PP-#60PW-MAPP) (Figure 4).

The response of a biocomposites to water soaking is related closely to the chemical and lignocellulosic anatomical properties of the bio-filler employed.<sup>34–38</sup> Employment of filler such as STDDGS results in a much larger increase in weight gain compared to employing PW filler (Figure 4). DDGS fillers contain more protein and less cellulose/lignin material than the PW fillers which maybe the reason for their higher absorbance rates (Figure 4). Overall, those combination composites containing high concentrations of DDGS exhibited higher weight gain than those combination composites containing less DDGS. For example, the PP-20PW/20STDDGS-MAPP composite exhibited the greatest weight gain, i.e., 9.5%; while the PP-12.5PW/

12.5STDDGS-MAPP composite exhibited only a 3.7% weight gain. Further work needs to be conducted to address the water absorbance situation in DDGS composites to determine if these materials can be effectively employed outdoors or in “wet” environments.

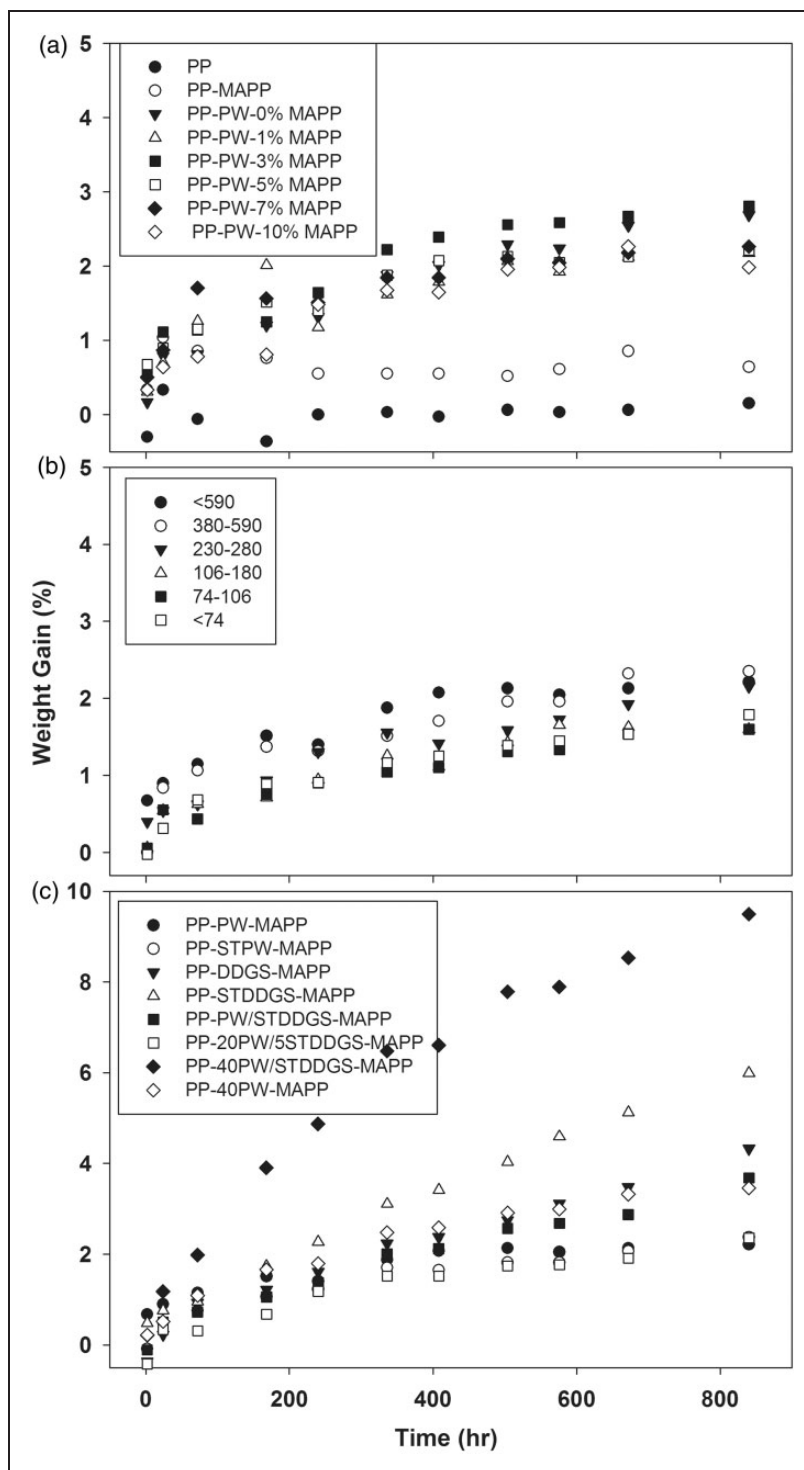
Environmental stresses such as water soaking may cause changes in the mechanical properties to occur which needs to be measured in order to assess the potential commercial value of a composite.<sup>37,38</sup> Flexural properties have been reported to decrease when LPC are weathered.<sup>18,37,38</sup> The mechanical properties of composites as well as neat PP and PP-MAPP may be affected by water soaking (Figure 5). Soaking caused  $\sigma_u$  values decreased 11% and 12% for neat PP and PP-MAPP, respectively, while %El values decreased 27% and 30% for neat PP and PP-MAPP, respectively. However, E values only decreased 3% and 4% for neat PP and PP-MAPP, respectively. Changes in the mechanical properties for the composites may change depending on the composition of the filler, particle size, or MAPP concentration employed (Figure 5). The  $\sigma_u$  and %El values for soaked composites slightly increased for composites containing higher MAPP concentrations while their E values slightly decreased (Figure 5). However, composites containing MAPP were less likely to show significant changes in mechanical properties than composites without MAPP (Figure 5). Soaked composites containing various PW particle sizes showed the same or slightly higher  $\sigma_u$  and %El values compared to the un-soaked composite blends. However, regardless of the particle size tested, the E values significantly decreased in the soaked composites compared to the not-soaked composites. The composites that exhibited the largest reductions in E values were those containing the largest particle sizes (PP-#40-MAPP and PP-#60-MAPP) with ~10% reductions.

All soaked PW, DDGS, or PW/DDGS combination-filler composites exhibited significant lower E values compared to the not-soaked composites (Figure 4). Soaked and un-soaked PP-25PW-MAPP and PP-40PW-MAPP composites retained their  $\sigma_u$  and E values. However, the soaked samples of PP-25STDDGS-MAPP and the combination filler composites (i.e., PP-12.5PW/12.5STDDGS-MAPP and PP-20PW/20STDDGS-MAPP) exhibited significant changes in their  $\sigma_u$  values compared to un-soaked bars. This trend is likely due to the concentration of DDGS present in these composite blends.

### Thermal analysis

Each bio-filler has its own unique structural and chemical properties which characterizes the peculiarities of the species and may be reflected in the thermal





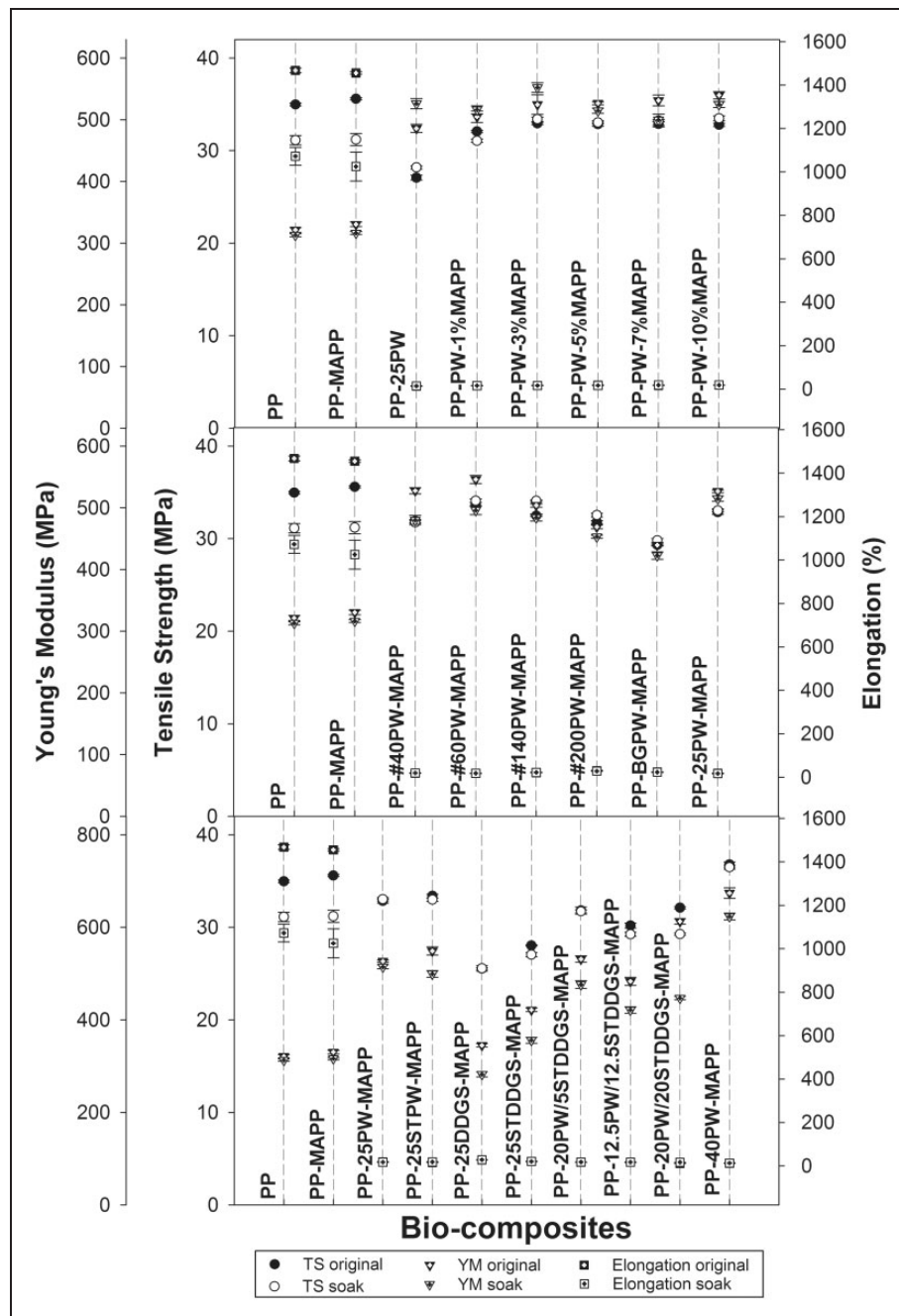
**Figure 4.** Comparative water absorption plots for various composites for 872 h of soaking. (a) Influence of MAPP concentration on PVF weight gain, (b) influence of PVF particle size on weight gain and (c) influence of filler mixtures on weight gain.

PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood; STPW: solvent-treated Paulownia wood; DDGS: dried distiller's grain with solubles; STDDGS: solvent-treated dried distiller's grain with solubles.

properties of the composite.<sup>18,39–43</sup> The thermal properties measured by DSC and TGA of the various PW and DDGS composite blends are shown in Table 3. Composite blends invariably exhibited higher  $T_m$  and

$T_c$  values compared to the neat PP or PP-MAPP values. The increase in  $T_m$  and  $T_c$  may be attributed to intermolecular interactions between the hydroxyl groups of the fillers and the carbonyl groups of the MAPP matrix.





**Figure 5.** Comparative mechanical properties for composites before and after 872 h of soaking.

PP: polypropylene; MAPP: maleated polypropylene; PW: Paulownia wood; STPW: solvent-treated Paulownia wood; DDGS: dried distiller's grain with solubles; STDDGS: solvent-treated dried distiller's grain with solubles.

Inclusion of increasing concentrations of MAPP in the composites had little influence of  $T_c$  and  $T_m$  values but resulted in distinctly higher  $\chi_c$  values compared to neat PP. For example, the  $\chi_c$  values of PP-PW-1%MAPP and PP-PW-5%MAPP were 4% and 9%, respectively, higher than the  $\chi_c$  values of neat PP. Particle size in PW composites had mixed influences on DSC thermal properties with no distinct trends apparent (Table 3).

Depending on their function as nucleating agents, the  $\chi_c$  values in LPC often differ from that of neat resin matrix.<sup>39,41,43</sup> The increase in  $T_m$  of the composites is likely related to the enhancement of the PP crystal lattice network by the presence of PW or DDGS particles which act as nucleation sites. Lower crystallization levels occurred in composite blends containing DDGS filler compared to using PW filler. For example,

a blend containing PP-25STDDGS-MAPP exhibited a crystallinity value that was 1% less than neat PP; and composite blend containing PP-20%PW/20%STDDGS-MAPP exhibited a crystallinity value that was 5% higher than neat PP. Other investigators have also observed a decrease in the  $\chi_c$  values associated with various LPC.<sup>43</sup> The presence of MAPP in the composite tended to increase crystallinity level of the composites.

The degradation of neat PP, occurs in a single stage, begins at 433°C, with a maximum decomposition rate occurring at 452.2°C. The PP degradation was 99.1% complete at end of this stage. Similarly, the PP-MAPP blend mimics these parameters. In contrast, there are several degradation peaks for the PW and DDGS composites. The initial degradation temperature of the DDGS flour was ~215°C and a prominent decomposition peak occurred at 250°C. This degradation peak is associated with the decomposition of low-molecular-weight components such as hemicellulose which degrades between 225°C and 325°C.<sup>10,43</sup> A second higher degradation peak occurs with a maximum at 316°C. This degradation peak is associated with decomposition of cellulose which degrades in the 300°C to 400°C range.<sup>44</sup> A third degradation peak corresponds to lignin decomposition is often reported occurring near 420°C; however, it is not seen in this study because it was obscured by the decomposition of the PP.<sup>44</sup> The PW and DDGS composites have residual weights that varied from 3.2% to 12.3% due to the heterogeneous ingredients of the fillers. Differences among the PW/DDGS composites' initial degradation temperatures were due to the association of the filler material and the plastic resin. Slightly higher initial degradation temperatures and peak temperatures occurred for STDDGS composites compared to the DDGS composites; this can be attributed to the occurrence of higher levels of low-molecular-weight organic compounds in DDGS composites compared to STDDGS composites. Similarly, other investigators report that occurrence of extractables in fillers decreased initial degradation temperatures.<sup>26</sup> The addition of different concentrations of MAPP or various PW particle sizes had little influence on the decomposing behavior of the PW composites. Based on the TGA analysis and since the injection molding temperatures did not exceed 200°C, both the PW and DDGS composites were relatively thermally stable for the temperatures they were subjected to in this study.

## Conclusions

The extrusion compounding and injection molding parameters to produce PP-PW composites with tensile and flexural properties that exceeded neat PP were

determined with respect to particle sizes and MAPP concentrations. PW could be blended into PP without a coupling agent (PP-25PW) to obtain a composite that exhibited  $\sigma_u$ , E, and  $E_b$  values that compared favorably to neat PP, while their elongation and impact strength values were significantly lower than neat PP. Testing a range of MAPP concentrations (0–10%) with PW composites resulted in selection of 5% MAPP as the choice concentration to be employed in future studies. Particle sizes of PW significantly affected mechanical properties of composites. PW composites containing particles below 250- $\mu$ m diameter exhibited reduced the  $\sigma_u$ ,  $E_b$ , and impact strength properties compared to compositions of PW composites that had larger particle sizes. PW composites containing a mixture of particles ( $\leq 600 \mu$ m) are recommended to be employed in WPC, since they provided excellent mechanical properties and were the easiest to manufacture. STDDGS composites (PP-25STDDGS-MAPP) exhibited tensile and flexural properties that exceed neat PP and PP-DDGS-MAPP composites. However, STDDGS composites were inferior to PW composites. Mixing STDDGS and PW fillers at various proportions resulted in novel combination composites that exhibited superior tensile and flexural moduli and impact strength properties compared to STDDGS composites. Water soaking for 872 h caused composites to exhibit an increase in weight gain but may alter their mechanical properties depending on the blend tested.

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## Conflict of interest

None declared.

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